Nov. 3, 1959 D. G. TIPOTSCH 2,911,532

ION COLLECTOR FOR MASS SPECTROMETRY

Filed March 26, 1956 2 Sheets-Sheet 1

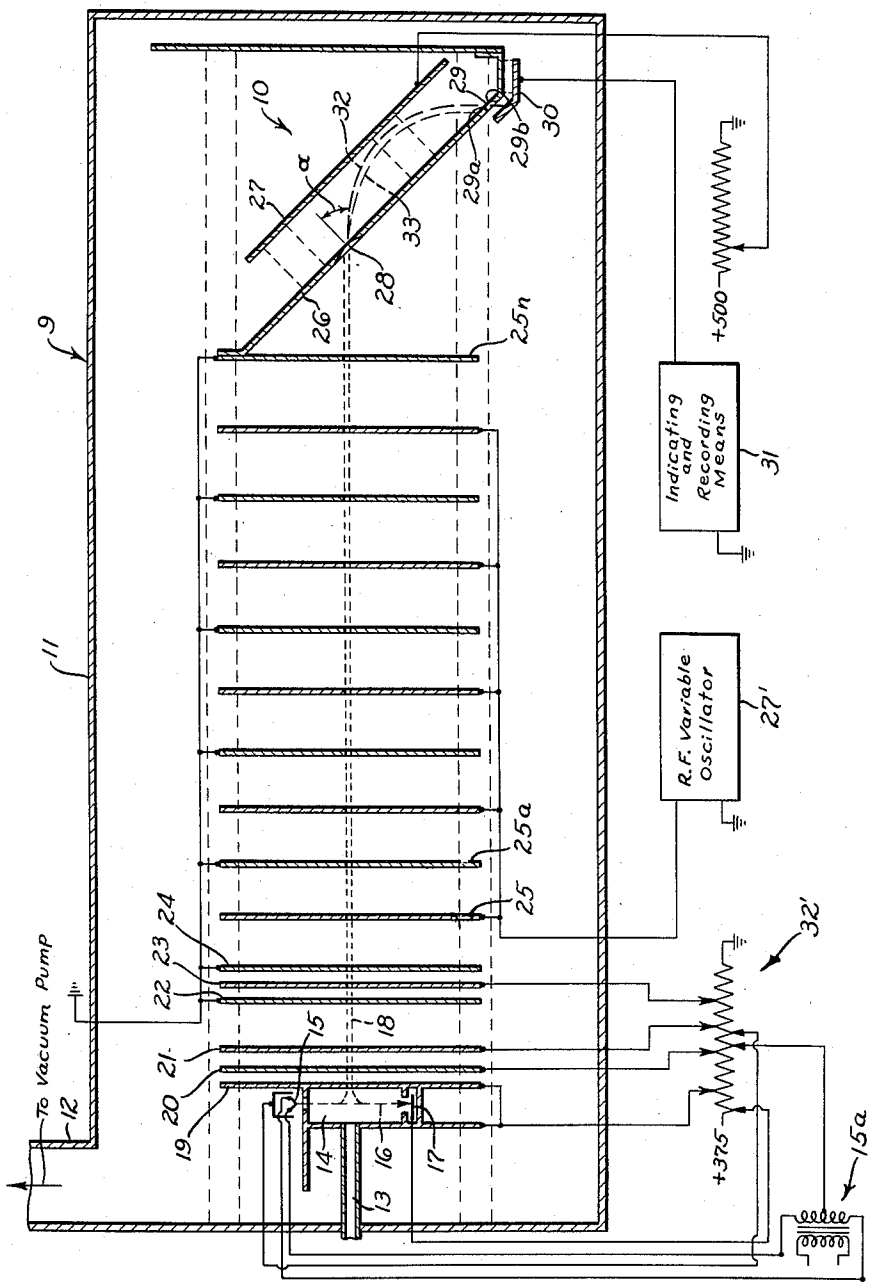

Fig. 1.

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Fig. 2.

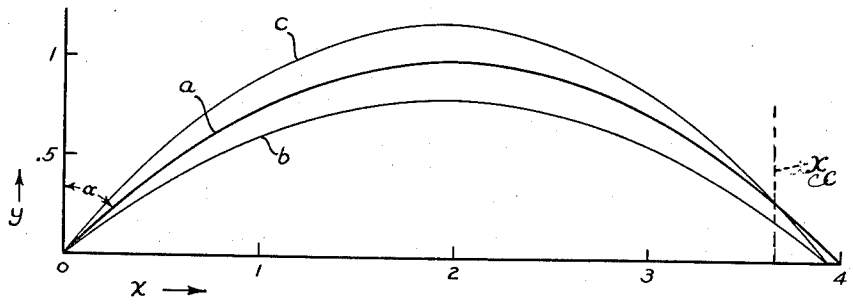


Fig. 3.

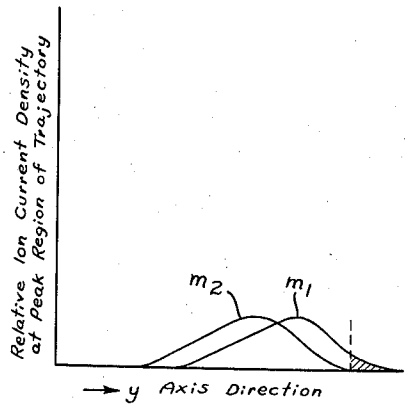
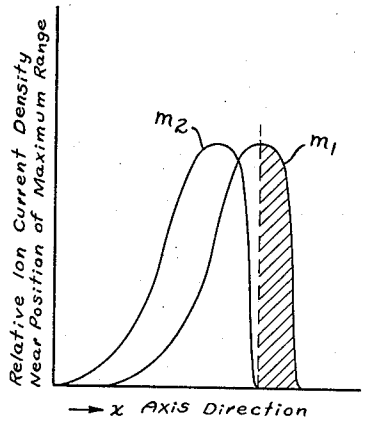


Fig. 4.



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2,911,532

ION COLLECTOR FOR MASS SPECTROMETRY

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5 Claims. (Cl. 250—41.9)

The present invention relates in general to mass spectrometry and, more particularly, to an ion collector for radio frequency mass spectrometers, which may, for example, be of the type disclosed and claimed in the copending applications of George H. Hare and David R. Margetts, Serial No. 370,582, filed July 27, 1953, and Serial No. 378,756, filed September 8, 1953, now U.S. Patent 2,769,093 granted October 30, 1956.

As general background, mass spectrometers of this general type include: an ion source; ion analyzer means for selectively varying the kinetic energies of the ions emitted by the source in accordance with their respective masses, or more accurately, in accordance with their respective charge-to-mass ratios; and selective ion collector means. The analyzer provides selected ions of a selected charge-to-mass ratio with an optimum kinetic energy level while providing nonselected ions of other charge-to-mass ratios with other kinetic energy levels differing from the optimum. The ion collector separates the selected ions from the non selected ions on the basis of the energy level differences produced by the analyzer means, the ion collector providing a collecting electrode, or collecting electrode means, for collecting the selected ions. The optimum kinetic energy level with which the selected or preferred ions are provided may be either a maximum or a minimum, the ion collector of the present invention having particular utility with an instrument which maximizes the kinetic energy of the preferred ions, although it is useful also with one which minimizes the kinetic energy thereof. Further, while the ion collector of the invention is particularly applicable to a radio frequency mass spectrometer, and is considered with particular reference to a radio frequency instrument herein, it will be understood that it may be utilized in any instrument which selectively alters the kinetic energy level of ions of a preferred mass, or preferred mass-to-charge ratio, relative to nonpreferred ions of other charge-to-mass ratios.

Basically, the operation of an ion collector of the type to which the present invention relates involves projecting the ion beam emerging from the analyzer means into a substantially uniform electrostatic deflecting field at an angle of substantially 45° to the equipotential planes of such field and at an initial position in a plane of low field potential so that the ions traverse planes of successively higher field potentials. The ions constituting the beam accordingly execute parabolic trajectories within the deflecting field space varying in altitude and range in accordance with the respective entrant kinetic energies thereof. An ion having a high entrant energy level tends to attain both a higher altitude and a greater range than one of low entrant energy. This variation in trajectory makes it possible to separate ions having a selected entrant kinetic energy from those ions having different entrant kinetic energies, the selected entrant energy level corresponding to the preferred charge-to-mass ratio.

In the ion collectors of this general character which are described in the aforementioned copending applications, the ions are separated on the basis of the maximum or peak altitudes they attain in the electrostatic deflecting field. For example, in one prior ion collector, used in an instrument which imparts the maximum energy level to the selected ions, these ions are collected at the crest of their parabolic trajectory by means of a collecting electrode which intercepts only the ions attaining the highest peak altitude, but which does not intercept ions having lower maximum or peak altitudes. On the other hand, if the analyzer means of the instrument is such that it imparts the minimum energy to the selected ions, an electrode is provided in the region of maximum trajectory altitude for intercepting all ions attaining higher altitudes than that of the selected ions, the latter attaining only a minimum peak altitude and clearing the mentioned intercepting electrode to impinge on a separate, collecting electrode.

The foregoing prior ion collectors take advantage of a focusing action which causes parallel, equal-energy rays of the ion beam to converge within a narrow band at the crest of the trajectory. The lateral separation of such parallel rays results from the finite width of the ion entrance aparture through which ions are admitted into the electrostatic deflecting field. However, it has been found that while this focusing action compensates effectively for lateral displacements of the selected ions in the ion beam, it does not compensate for slight deviations in the angle at which the selected ions, or any single-energy ions, enter the deflecting field. In fact, the effect of such entrant angle deviations on resolution, and on the useful ion current obtainable at the collecting electrode, may be much more serious than the effect of lateral spacing due to the width of the entrance aperture. Thus, in an instrument wherein the maximum energy is imparted to the selected ions, it is possible for ions of lower energy than that of the preferred ions to impinge on the collecting electrode if they enter the field at an angle of less than 45° with respect to a line perpendicular to the equipotential planes of the field. Similarly, in an instrument which imparts the minimum energy to the preferred ions, ions of an energy higher than the selected ions, but entering the deflecting field at an angle of more than 45°, may miss the intercepting electrode adapted to block the nonpreferred ions and may impinge together with the preferred ions on the collecting electrode. In either event, mass resolution is seriously impaired. In some instances (in instruments wherein selected ions attain maximum energy) it has been necessary in order to fully resolve adjoining masses above mass 40, for example, to reduce the deflecting potential and accept only the 10% of the available ions of the selected mass which attain the maximum trajectory altitude and which are free from interfering ions of the adjoining mass. Obviously, this drastically reduces the ion current available at the collecting electrode.

Another disadvantage of prior ion collectors which operate on the basis of ion trajectory altitudes is that when a mass spectrum is scanned, i.e., when the instrument is made responsive to successive masses as by varying the resonant frequency in radio frequency instruments, the ions of successive masses may enter the ion collector at a continuously varying angle, the reasons for this phenomenon being only incompletely understood at the present time. Thus, when collecting on the basis of variations in trajectory altitude with ion mass, the proportion of the preferred ion beam collected varies somewhat with mass. This would not be objectionable except for the fact that it is desirable to vary the deflecting potential in order to change the resolution, e.g., in order to collect a larger portion of the available current where the mass resolution is inherently high, as at low mass numbers. When this is done, it is found that the fractionating pattern, or distribution of ion fragments of various masses

for a given simple molecule, changes also. For maximum operating convenience however, this should remain independent of resolution.

A primary object of the present invention is to eliminate the foregoing and various other disadvantages of prior ion collectors, irrespective of the type of mass spectrometer with which the ion collector of the invention is used.

More particularly, an important object of the present invention is to provide an ion collector which separates the selected ions from the nonselected ions on the basis of the differences in the range of the trajectories which the ions execute, instead of on the basis of the differences in the altitudes thereof.

In other words, an important object of the present invention is to separate the selected and non-selected ions at the ends of their trajectories within the deflection space, instead of at the crests thereof. As will be shown hereinafter, variations in trajectory range with variations in entrant angle are much smaller than variations in trajectory altitude with such angular variations. This permits the ion collector of the invention to achieve superior resolution and increased ion current, these being important features of the invention.

Another object of the invention is to provide an ion collector which includes electrode means defining a substantially uniform electrostatic deflecting field, means for admitting ions into such field in a beam at a mean inclination of substantially 45° to the equipotential planes of the field and at an initial position in a plane of low potential, whereby ions of different masses execute different trajectory ranges in returning to terminal positions in a plane of substantially the same low field potential, means adjacent the terminal position of the trajectory range executed by the selected ions for intercepting ions deviating therefrom in range by more than a predetermined small amount, and collecting electrode means adjacent such intercepting means for collecting selected ions which are not intercepted by the intercepting means.

A further object is to provide an ion collector which includes two spaced, parallel electrodes disposed at an angle of substantially 45° to the ion beam, one of these electrodes being maintained at a lower potential than the other to provide a substantially uniform electrostatic deflecting field therebetween. A related object is to provide the lower-potential electrode with an ion entrance aperture and to provide it with an ion intercepting edge spaced from the ion entrance aperture, such ion intercepting edge preferably being formed as an edge of an ion exit aperture. Still another object is to provide an ion collecting electrode external to the space between the deflecting electrodes and so positioned with respect to the ion exit aperture that ions not intercepted by the ion intercepting edge of such deflecting electrode impinge on the collecting electrode as a beam of substantially selected ions only.

The foregoing objects, advantages, features and new results of the present invention, together with various other objects, advantages, features and new results thereof which will be evident to those skilled in this art in the light of the present disclosure, may be attained with the exemplary embodiment of the invention illustrated in the accompanying drawings and described in detail hereinafter. Referring to the drawings:

Fig. 1 is a semidiagrammatic, longitudinal sectional view of a mass spectrometer which incorporates the ion collector of the invention;

Fig. 2 is a graph comparing variations in ion trajectory altitude and ion trajectory range with variations in entrant angle into an electrostatic deflecting field;

Fig. 3 is a graph illustrating the distribution of ion current density in the region of the ion trajectory peaks in the electrostatic deflecting field; and

Fig. 4 is a graph illustrating the variation in ion current density near the position of maximum ion trajectory range in the electrostatic deflecting field.

An instrument **9** embodying an ion collector **10** of the present invention is illustrated in Fig. 1 of the drawing, this instrument being similar in principle to that described in said applicaton Ser. No. 370,582. The means for ionizing the sample, for imparting different energies to the ions of different mass, and for collecting a selected ion species are enclosed in a vacuum-tight housing **11** connected to a vacuum pumping system, not shown, via a duct **12**. More specifically, the sample, in the form of a gas or vapor, is introduced into an ion chamber **14** at a suitable pressure through an inlet tube **13**. A filament **15** powered by a transformer **15***a* provides an electron stream **16** which is directed through the ion chamber **14** and collected by a positively charged electrode **17**. A portion of the sample material is ionized under bombardment by the electron stream. Two sets of perforated electrodes, **19** to **21**, and **22** to **24**, connected to points of suitable potential on a power supply **32'**, draw the ions out of the ion chamber, giving them an initial acceleration and collimating them into a narrow beam **18**. The perforations in these and all subsequent electrodes may either be holes or, preferably, elongated slits. Thus, Fig. 1 may be interpreted as showing slits which are oriented perpendicularly to the plane of the drawing. In this case, however, it would be preferable to reorient the electron beam so that it too is perpendicular to the plane of the drawing.

The ion chamber **14**, the electron beam forming means **15**, **17** and the electrodes **19** to **24** constitute what may be termed the ion source. This is followed by a so-called analyzer means or analyzer section which comprises an array of perforated plates, **25**, **25***a*, . . . **25***n*, connected alternately to one terminal of a variable radio frequency oscillator **27'** and an oscillator return point. e.g., ground, as shown. For a given accelerating potential at the ion source, and any given frequency and amplitude of the radio frequency oscillator **27'**, only particles of a particular mass, or, strictly speaking, of a particular charge-to-mass ratio, will pass through the analyzer plates in resonance with the radio frequency signal. Ions of this selected mass are accelerated in phase with the alternating voltage through each of the successive analyzer stages and thus acquire a maximum kinetic energy, whereas particles of different mass, higher or lower, fall out of phase and either do not emerge from the analyzer section or, at best, emerge with energies less than that of the preferred particle.

The ion collector **10** of the invention comprises two parallel electrodes or plates **26** and **27** inclined at an angle of substantially 45° to the entrant ion beam **18**. The base plate **26** is at a low potential, for example, ground, and may be connected to the last analyzer plate **25***n* as shown. The plate **27** is at a relatively high potential, e.g., about one-half the ion beam energy in electron volts, or about 500 volts. Thus, there is provided between the plates **26** and **27** a substantially uniform electrostatic field having a plane of minimum field potential at the base plate **26**. The ions from the analyzer section enter the space between the plates **26** and **27** through a relatively narrow entrance slit **28** in the plate **26**, each ion traversing a parabolic trajectory and returning to the base plate **26**, where ions of the predetermined charge-to-mass ratio pass through an ion-selective exit slit **29** in the plate **26** positioned at the point of maximum range. Particles traversing the slit **29** impinge on a collecting electrode or electrode means **30** at or near ground potential. Ions of lower or higher mass, and therefore of lower energy, fall short of the slit **29** and impinge on an ion intercepting means formed by the base plate **26** adjacent an edge **29***a* of the slit **29**. The numerals **32** and **33** represent, respectively, the paths of preferred and nonpreferred ions. An indicating and/or recording means **31**, connected to the electrode **30**, indicates and/or records the relative abundance of the selected ions.

The ion collector **10** operates on the principle that, for ions of any given energy, those which enter at 45° attain the maximum range. Particles of the same given

energy, but of an initial entrant angle either larger or smaller than 45°, return to the base plate **26** within a shorter distance. However, the variation in range, for varying entrant angle, is extremely small compared with the corresponding variation in the maximum attained altitude. Accordingly, by collecting at the position of maximum range, the overlapping of the paths of ions of adjacent masses due to deviations in the entrant angle, when more than one ion species enters the collector, is greatly reduced and resolution and useful ion current are corrpesondingly increased.

The foregoing principle is illustrated in Fig. 2. The origin, lower left, corresponds to a point on the entrance slit **28**, and the base line $y=0$ corresponds to the surface of the base plate **26**. The curve *a* is the trajectory of a particle entering at $\alpha=45°$, and the curves *b* and *c* are the trajectories for particles of the same energy deviating in either direction by 0.1 radian, or about 5.7°. This is a relatively large angular deviation and is shown for purposes of illustration only. Taking the peak trajectory value of y for $\alpha=45°$ as unity, the range, or maximum value of x, is 4. For particles entrant at any angle α,

$$x=v_0 t \sin \alpha,$$

and

$$y=\tfrac{1}{2} at^2+v_0 t \cos \alpha,$$

where v_0 is the entrant velocity, t is time and a is the acceleration, a being equal to $-Ee/m$ where E is the deflecting field strength, and e/m the ionic charge-to-mass ratio.

Eliminating t, expressing a in terms of the deflection field and v_0 in terms of the effective total voltage V accelerating the ion before entering the collector **10**, the following equation results:

$$y=\frac{-Ex^2}{4V \sin^2 \alpha}+\frac{x}{\tan \alpha}$$

It is found that y has a maximum value, or altitude, at the peak of the trajectory given by

$$y_{max}=\frac{V \cos^2 \alpha}{E}$$

and that x_{max}, or maximum range, is

$$x_{max}=\frac{4V}{E} \sin \alpha \cos \alpha$$

The trajectory for a value of α less than 45° crosses the trajectory for $\alpha=45°$ at a value of x given by

$$x_c=\frac{-4V}{E}\left(\frac{\cos \alpha-\sin \alpha}{2 \sin \alpha-\csc \alpha}\right)$$

The incremental changes of maximum altitude and range with change of initial angle are respectively given by

$$\frac{dy_{max}}{d\alpha}=\frac{-V}{E} \sin 2\alpha$$

and

$$\frac{dx_{max}}{d\alpha}=\frac{4V}{E} \cos 2\alpha$$

It is noted that at $\alpha=45°$, $dx_{max}/d\alpha$ is zero, i.e., x is a maximum, and that for even relatively large deviations from $\alpha=45°$, only very small changes in x_{max} may be expected. On the other hand, $dy_{max}/d\alpha$ has a finite value at $\alpha=45°$, and for given deviations of α, the deviation in y_{max} may be many time that of x_{max}. This is borne out in Fig. 2, where, for the entrant angle deviation of ± 0.1 radian, the total deviation in y_{max} is 0.396, and the total deviation of x_{max} is only 0.08, a ratio of approximately five to one. Taking smaller angles of deviation, closer to those encountered in practice, the ratio of the total deviation of y_{max} to that of x_{max} is rapidly increased. Thus, at a deviation of $\pm 1°$, total deviations in y_{max} and x_{max} are 0.068 and 0.0024, respectively, a ratio of approximately 28 to 1.

It will be noted that for any pair of rays deviating in entrant angle symmetrically from 45°, the deviation in y_{max} is symmetrical, and the range, or x_{max}, values are identical. Thus the curves *b* and *c* of Fig. 2 have a common terminus on the x axis.

Other conditions being equal, the collector **10** of the present invention makes possible, in a typical instrument of the type described, an increase in the ion signal current by a factor of five or more, or for the same current, a substantial increase in resolving power, The reason for the current gain is explained by the schematic curves of Figs. 3 and 4. In Fig. 3, the curves m_1 and m_2 show the ion current density distribution, attributable to each of two adjoining masses, along the "vertical" or y direction, in the vicinity of the trajectory peaks, where prior ion collectors have operated. The preferred mass is represented by m_1 and, for simplification, the relative total abundance of the masses is assumed equal. The long "skirts" on these curves are largely the effect of ions entering the deflection space at angles which deviate in either direction from 45°. To obtain a signal for the ion m_1 which is substantially independent of the ion m_2, only that portion of the m_1 current may be collected which falls to the right of the dotted line and is indicated by the shaded area. Thus, because the right-hand skirt of m_2 overlaps a major portion of the range of m_1, only a small portion of m_1 may be collected to give a useful signal.

Fig. 4 shows the improvement achieved in the present invention by collecting in the region of maximum range. Since the distribution for each ion species tails off primarily in one direction only, i.e., to the left as shown in this figure, a much larger portion of the available current of the preferred ion, again shown by the shaded area, may be collected without interference by the adjoining ion. The leading (right-hand) edges of the curves of Fig. 4 are not perfectly vertical because particles of a given mass entering the collector **10** at 45° vary slightly in energy, and because of the particular shape of the energy distribution curve for such particles.

The effect of the invention is that aberration due to angular deviation is no longer a dominant factor in restricting attainable resolution or ion current. Instead, this effect is made at least comparable to, and usually smaller than, other effects which limit performance, such as energy separation of adjacent mass peaks, energy spread for a given mass, collector slit-width effects, etc.

Referring again to Fig. 1, it will be seen that additional advantages result from the fact that the collecting or sensing electrode **30** is now adjacent the deflection plate, **26**, which is at the lower potential, i.e., at or near ground potential, rather than near the high voltage plate **27**. For example, transients formerly appearing when the deflection voltage was changed, due to capacitive coupling between the deflector plate and the sensing electrode, are substantially eliminated. The fractionating pattern becomes substantially independent of the deflection voltage, because of the relative insensitivity to variations in the entrant angle. Moreover, the electrostatic deflection field in the vicinity of the sensing electrode **30** is now substantially free of distortion, and this further improves resolution. Additionally, the problem of electrical leakage between the relatively high-potential deflection electrode and the low-potential sensing electrode is substantially eliminated, since the sensing electrode now adjoins the deflection plate of lower potential. Finally, the lower potential deflection plate **26** may, if desired, be made about 20 volts negative with respect to the collector electrode **30**. This permits the plate **26** to act as a suppressor for secondary electrons originating at the collector electrode **30** by returning them to this electrode.

Because the present invention increases the ion current available at the sensing electrode, it is possible, if

desired, to reduce the width of the entrance slit **28** appreciably, and thereby reduce the lateral spread in initial ion position. A suitable entrance slit width may be 0.015 inch. The collector or exit slit **29** is made somewhat larger, e.g., 0.040 inch, so that the beam of preferred ions may still impinge on the collector electrode **30** despite any residual angular deviation effect and the small energy spread for preferred ions entering at 45°. The resolution, in general, of the collector **10** is a function of the ratio of the entrance slit width to the distance between the slits **28** and **29**.

It will be apparent that the significant functional portion of the exit slit **29** is the inner edge **29***a* thereof. For example, the base plate **26** could terminate at **29***a*, and the outer edge, **29***b*, of the slit could be omitted. In general, however, it is desirable to use an actual slit and thereby maintain a more nearly undisturbed deflection field in the exit slit region.

It will be apparent also that in a mass spectrometer where the analyzer section decelerates the selected ions instead of accelerating them, the collector of the invention may also be useful in certain cases. The exit slit or exit slit edge of the collector in this case is positioned to select ions of minimum, rather than maximum, energy.

Although I have disclosed an exemplary embodiment of my invention herein for purposes of illustration, it will be understood that various changes, modifications and substitutions may be incorporated in such embodiment without departing from the spirit of the invention as defined by the claims hereinafter appearing.

I claim as my invention:

1. In an ion collector for an ion sorting device comprising an ion source and analyzer means for imparting maximum energy to selected ions of a particular charge-to-mass ratio emitted from said source relative to non-selected ions emitted therefrom; the combination of: means providing a substantially uniform electrostatic deflecting field; means for admitting a beam of ions from said analyzer means to said field at a mean inclination of substantially 45° to the equipotential planes of said field and at an initial position in a plane of low field potential, the ions of said beam executing varying trajectories in said field and returning to terminal positions in a plane of substantially the same low field potential, said selected ions attaining a particular, maximum range greater than the range executed by said non-selected ions; means adjacent the terminal position of said maximum range for intercepting ions executing ranges shorter than said maximum by more than a predetermined small amount; and collecting electrode means adjacent said intercepting means for collecting substantially only said selected ions.

2. An ion collector as defined in claim 1 wherein said means providing said deflecting field comprises a pair of spaced, parallel electrodes and means for maintaining said electrodes at different electrode potentials, respectively, said ion admitting means including an ion entrance aperture in that electrode of said electrode pair which is at the lower of said electrode potentials.

3. An ion collector as defined in claim 2 wherein said ion intercepting means comprises an ion intercepting edge of said lower-potential electrode.

4. An ion collector as defined in claim 3 wherein said ion intercepting edge comprises an edge of an ion exit aperture located in said lower-potential electrode and spaced from said ion entrance aperture.

5. An ion collector as defined in claim 4 wherein said collecting electrode means is located external to the space defined by said electrodes and adjacent to said ion exit aperture.

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